

Preparation and Properties of Films and Fibers of Disordered Cellulose

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Synopsis

The preparation and properties of films and fibers of highly disordered cellulose are described; the basis of the preparation is the regeneration of cellulose from cellulose derivatives in non-aqueous media. These celluloses are at least 97% hydrogen-bond disordered (as measured by the infrared-deuteration technique), give x-ray diagrams showing poor three-dimensional order, and are practically completely accessible to swelling agents such as water and formic acid. The crystallization of these disordered celluloses is described. The effects on native cellulose of ball milling, mercerization, amine treatment, swelling in acid and salt solutions, and swelling in solutions of potassium hydroxide in non-aqueous solvents are described with reference to changes in fine structure as measured by the infrared-deuteration technique.

INTRODUCTION

The primary purpose of this paper is to consider in detail a method of preparing films and fibers of highly disordered cellulose and to describe some properties of these materials. Subsidiary parts of the paper contain descriptions of the effects of grinding treatments and various swelling treatments (e.g., mercerization, amine treatments) on the disorder in native celluloses.

The infrared-deuteration technique is the principal method employed to characterize and measure the disorder present in the various samples of cellulose. In this technique,¹⁻³ the hydroxyl groups in the cellulose are separated into two fractions, one fraction being readily accessible to, and exchanging readily with, deuterium oxide, the other fraction being relatively inaccessible to deuterium oxide and thus exchanging slowly and incompletely. The slowly accessible and inaccessible hydroxyl groups have been shown to be hydrogen-bonded in a regular ("crystalline") manner, giving rise to an infrared, hydroxyl stretching band containing characteristic peaks and shoulders. The fraction of the hydroxyl groups readily accessible to, and exchanged by, deuterium oxide has been shown to be hydrogen-bonded in a more or less disordered manner, and thus the hydroxyl stretching band arising from these hydroxyl groups is broad and featureless. This "disordered" hydroxyl band is removed during the rapid stage of the deuteration, being replaced by a similarly featureless band in

TABLE I

No.	Type of cellulose and treatment	Hydrogen-bond order, % ^a	Type of ordered regions ^b
1	Disordered cellulose		
2	Prepared from cellulose acetate	0-3	II?
3	“ “ xanthate	0-3	II?
3	“ “ cuprammonium	3-5	II?
4	Disordered cellulose from acetate		
4	H ₂ O at 20°C., 5-10 sec.	15	II
5	“ “ 100°C., 5-10 min.	25	II
6	Ethanol-water 90/10 (v/v)	10	Imperfect II?
7	“ “ 70/30 (v/v)	15-20	Imperfect II?
8	Disordered cellulose from acetate, never dried		
8	Acidified DMF, then DMF	5-10	IV?
9	“ “ “ H ₂ O, 20°C.	20	IV?
10	“ “ “ H ₂ O, 100°C.	25	IV + II?
11	Viscose film		
11	Untreated	25	II
12	2-3 <i>N</i> NaOH, 20°C.; washed H ₂ O, 20°C.	25-30	II
13	“ “ “ washed EtOH	5-15	II
14	“ “ “ acidified EtOH or acidified DMF	20-25	II
15	Bacterial cellulose		
15	Untreated	65	I (type A)

16	5 <i>N</i> NaOH, 20°C.; washed H ₂ O, 20°C.	35	II (+ I)
17	" " washed EtOH	5-15	II
18	" " washed acidified EtOH or acidified DMF	10-25	II
19	Ethylamine, 0°C. for 30 min.; chloroform-extracted	45	I (type B)
20	" " " " evaporated	45	I + III
21	98% Ethylenediamine 20°C. for 4 hrs.; evacuated, water-extracted	40-45	I (type B)
22	" " DMF-extracted	25	I (type B)
23	65% (w/w) aqueous H ₂ SO ₄ , 20°C., 1 min.	40	II?
24	66% (w/w) aqueous HNO ₃ , 20°C., 10 min.	35	II
25	Saturated aqueous Ca(SCN) ₂ , 20°C., 16 hr.	40-45	I + II
26	73-74% (w/w) aqueous ZnCl ₂ , 20°C., 16 hr.	65	I (type A)
27	10% (w/w) KOH in butanol or 5% (w/w) KOH in 1:1 butanol-kerosene	20-40	I (type B)
Cotton			
28	Untreated	58-60	I (type B)
29	5 <i>N</i> NaOH, 20°C.; washed H ₂ O, 20°C.	35-40	II + I
30	" " " " washed ethanol	15-25	II
31	" " " " washed acidified EtOH or acidified DMF	20-35	II
32	Milled 20 min.	40	Mainly I
33	" " 60 min.	15	Mainly I
34	" " 120 min.	10	I + unknown
35	" " 240 min.	5	Unknown

^a All results suffer from uncertainty due to measuring error and, especially, sample variability; in some cases the results can be best expressed as a range of values, while in other cases it is preferable to express them as approximate single value.

^b Judged from the shape of the OH band of the hydrogen-bond ordered regions (i.e., after deuteration of the disordered regions).

the OD region of the spectrum and leaving in the hydroxyl region the band of the hydrogen-bond ordered hydroxyl groups.

The terms "order" and "disorder" as used here are, unless otherwise stated, as defined and measured by the infrared-deuteration technique. The highly disordered celluloses that are the main subject of this paper are celluloses that are highly disordered (as much as 99% in some instances) on this definition.

PREPARATION OF HIGHLY DISORDERED CELLULOSE FILMS AND FIBERS

The principle of methods of preparing cellulose films and fibers containing more than 97% disordered material is to regenerate the cellulose structure in a non-aqueous medium (from a cellulose derivative, or a solution of cellulose) and wash the regenerated cellulose in a nonaqueous solvent. Methods of this type were first described in some early work of Sisson^{4,5} and Ingersoll,⁶ and Manley⁷⁻⁹ has recently published information on disordered celluloses prepared in this way.

From Cellulose Aliphatic Esters

Fibers or films of cellulose esters (acetates or higher esters) are saponified in a dilute solution of caustic alkali in a short-chain aliphatic alcohol; the regenerated product is washed for several days in alcohol and dried in air. The precise nature of the ester, the alkali, and the alcohol, and the concentration and temperature of the saponifying solution do not seem to have any marked effect on the disordered nature of the final product. Both sodium hydroxide and potassium hydroxide have been employed as saponifying agents; alcohols in the range methanol to *n*-butanol appear to be equally efficient; and alkali concentrations from 0.25-2% by weight and temperatures of saponification from room temperature to 60°C. have been investigated. Treatment of secondary cellulose acetate in a 1% solution of sodium hydroxide in ethanol for 1 day at room temperature, followed by a prolonged wash in ethanol, was the usual procedure adopted for preparing disordered celluloses of this type. With care in preparation, these regenerated celluloses contained at least 97%, and often more than 99%, hydrogen-bond disordered cellulose (see Table I).*

Oriented films and filaments of hydrogen-bond disordered cellulose can be prepared by the non-aqueous saponification of oriented secondary cellulose acetate. This latter is made by stretching acetate film or filaments to draw ratio of 2 or 3 while swollen in 80/20 (v/v) methylene chloride-benzene; after evaporating this swelling agent, the oriented film or filament is given a further stretch, to a total draw ratio of 10-15, while swollen in an aqueous solution of 2 g./100 ml. phenol, 2 g./100 ml. sodium sulfate at 60°C., followed by washing in water.^{10,11}

*All values for per cent ordered or disordered cellulose given in the text are also listed in Table I (as per cent ordered cellulose, for clarity).

From Sodium Cellulose Xanthates

Regeneration of cellulose from sodium cellulose xanthate in non-aqueous solutions also gives products that are at least 97% disordered. The films of xanthate (viscose dope) on glass plates are coagulated in a 10 g./100 ml. solution of ammonium sulfate in water and regenerated in disordered form in a 10 g./100 ml. solution of sulfuric acid in ethanol. The film is washed in ethanol and dried in air.

From Solution in Cuprammonium Hydroxide

Solutions of cellulose in cuprammonium hydroxide, spread into film on glass plates, are precipitated by immersion in ethanol or in a dilute solution of mineral acid in ethanol. The product, after a prolonged wash in ethanol and drying in air, is at least 95% hydrogen-bond disordered.

Use of Partially Non-aqueous Systems and the Exchange of Disordered Cellulose to Other Non-aqueous Solvents

As would be expected from the above, celluloses containing intermediate amounts of hydrogen-bond order can be made by saponifying and washing the acetate in suitable mixtures of water and solvent; the amount gradually increases from about 3% in the absence of water, to about 20% in a 50/50 (v/v) mixture, and to about 25% in pure water.

Samples of disordered film, regenerated from secondary acetate in ethanol and washed in ethanol, were exchanged without intermediate drying to a variety of organic liquids; acetone, chloroform, pyridine, benzene, *n*-hexane, dimethylformamide, and formic acid were studied. The liquids were then evaporated from the films, under vacuum in the later stages of the evaporation. With the exceptions of the films exchanged to dimethylformamide and formic acid, the dried films were as disordered as the films dried from the ethanol. Prolonged immersion in formic acid dissolved the film, as described elsewhere;¹² a shorter immersion produced a significant proportion of ordered material.¹² Exchange of the never-dried disordered cellulose to dimethylformamide produced an interesting type of hydrogen-bond order in the cellulose structure, as described in a later section.

STRUCTURE AND REACTIVITY OF HIGHLY DISORDERED CELLULOSE

Disordered cellulose prepared from secondary cellulose acetate was used in these investigations. Unless otherwise stated, the secondary acetate was in the form of film cast on glass from solution in acetone.

Infrared-Deuteration Studies

The experimental procedures involved in the infrared-deuteration technique have been described elsewhere.¹⁻³ The cellulose is evacuated to dryness, reacted with deuterium oxide vapor (saturated or at a lower relative humidity) for a length of time sufficient to exchange the hydrogen-

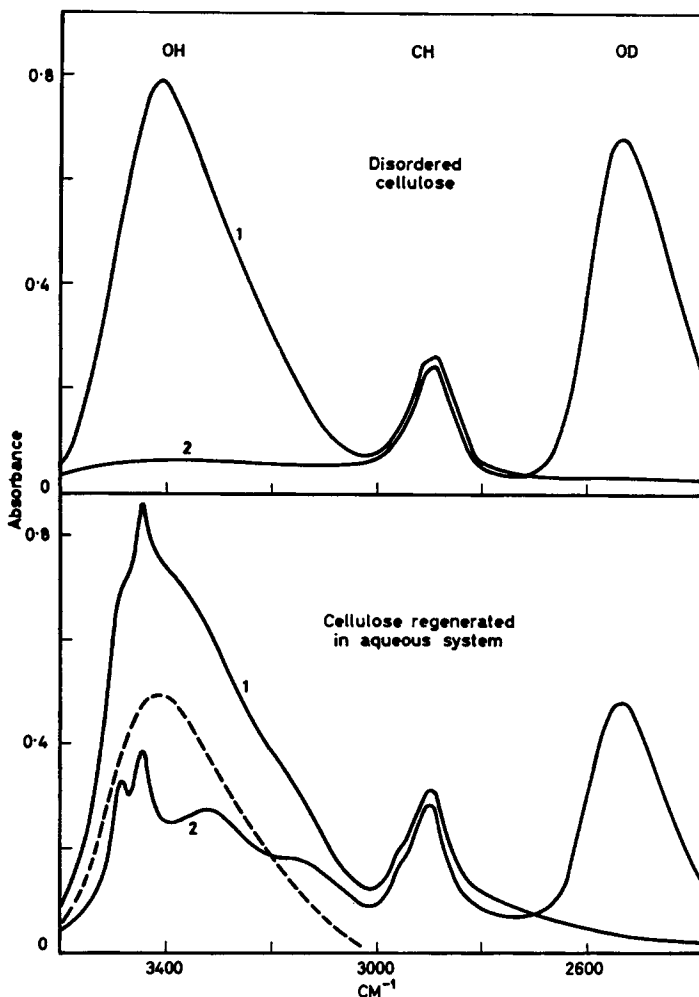


Fig. 1. Deuteration of disordered cellulose: (1) before deuteration; (2) after deuteration for 15 min. in saturated D_2O vapor at 20°C .; (---) band obtained by subtracting band 2 from band 1 (i.e., the hydrogen-bond disordered component).

bond disordered regions, and finally re-evacuated to dryness. The infrared spectrum of this film in the $3\ \mu$ region is measured on a Grubb-Parsons DB1 double-beam spectrometer with a lithium fluoride prism; it is emphasized that all spectra illustrated in this paper refer to vacuum-dried samples. With ordinary, partially ordered cellulose, the small amount of ordered material exchanged during this deuteration procedure is estimated by rehydrogenating the cellulose in 57% R.H. water vapor; any deuterated ordered material will resist rehydrogenation under these conditions.¹⁻³

With suitable calibration,^{2,3,13} the fraction of ordered cellulose can be calculated from the absorbances of the hydroxyl and OD bands at the end

of the exchange of the disordered regions. In the present work, the absorbances of the OH band near 3350 cm.^{-1} and the OD band at its peak near 2530 cm.^{-1} are measured relative to that of the CH band near 2900 cm.^{-1} , to eliminate the effect of variation in the thickness of the samples.

The infrared-deuteration behavior of disordered cellulose film is compared in Figure 1 with that of a cellulose film regenerated in aqueous solutions. The hydroxyl-stretching band of the undeuterated disordered film shows that practically all the hydroxyl groups are hydrogen-bonded, as with ordinary partially crystalline films, i.e., there is a little absorption in the $3600\text{--}3650\text{ cm.}^{-1}$ region. The hydroxyl band is broad and featureless. At least 97% of the hydroxyl groups react rapidly with saturated deuterium oxide vapor, and the hydroxyl band is replaced by a broad OD stretching band (Fig. 1). The weak hydroxyl band remaining after this rapid deuteration (corresponding to 0–3% of the OH groups) sometimes shows signs of the band shape characteristic of cellulose II ordered regions, but is often of a broad, poorly defined nature, with a peak in the 3440 cm.^{-1} region (as in Fig. 1). The spectrum of the aqueous-regenerated film after deuteration of the disordered regions (Fig. 1) illustrates for comparison the magnitude and shape of the hydroxyl band of the cellulose II ordered regions in an aqueous-regenerated cellulose. This particular sample contains about 25% ordered material, which is a value typical of celluloses of this type. The four peaks in the band are particularly well resolved in this example; most aqueous-regenerated celluloses give a less well resolved band, but the peaks are at similar frequencies and of roughly similar relative intensity. The hydroxyl band of the hydrogen-bond disordered component of the aqueous-regenerated sample (obtained by subtracting the hydroxyl band after deuteration from that before deuteration) is seen to be similar in shape and peak frequency to the hydroxyl band of the disordered cellulose (Fig. 1); likewise the OD band is similar to the OD band of the deuterated disordered cellulose. These facts strongly suggest that the nature of the hydrogen-bond disorder in the disordered cellulose is similar to that present in the disordered regions of ordinary regenerated celluloses.

Since the deuteration of disordered cellulose in saturated vapor causes a partial recrystallization of the cellulose, the OD bands of deuterated samples usually contain a small cellulose II component (not shown on the OD band in Fig. 1). This crystallization can be prevented by deuteration in vapor of lower humidity.

The oriented films prepared by the non-aqueous saponification of oriented acetate films are found to be as highly hydrogen-bond disordered, and as readily deuterated, as the ordinary glass-cast film after non-aqueous regeneration. The hydroxyl band shape is similar to that of the disordered film shown in Figure 1. Thus high orientation, as measured by either birefringence (values as high as 0.045) or x-ray diffraction does not, of itself, lead to a high degree of hydrogen-bond order. The hydroxyl-stretching band of these highly oriented films is found to be markedly dichroic in a way

somewhat similar to the hydroxyl band of the disordered component of oriented, partially ordered celluloses.¹⁴

It is interesting to note that the values for the accessibility to heavy water obtained with the present disordered films (97–100%) is distinctly higher than the accessibility value (90%) obtained on similarly prepared materials by a tritiation technique.⁸

X-Ray Diffraction Studies

The x-ray diffraction diagrams of disordered celluloses¹⁵ are similar in character to those obtained by Ingersoll⁶ and Manley.⁸ The diagrams show that the disordered cellulose, whether oriented or not, has only poor three-dimensional order. The oriented samples give short, but diffuse, arcs on the x-ray diagram, showing that the samples are, in fact, highly oriented but also of a low degree of lateral order.

Moisture Regain Measurements

A sample of disordered cellulose absorbed 16.75 g. water/100 g. dry cellulose at 57% R.H., 20°C. This compares with 17.0 g./100 g. calculated for this sample (98% hydrogen-bond disordered) on the basis of the known relation between hydrogen-bond disorder and moisture regain,⁸ and confirms that the nature of the hydrogen bond disorder in these highly disordered celluloses is similar to that present in ordinary, partially crystalline celluloses.

Formylation

The formylation behavior of disordered cellulose when immersed in formic acid indicates that this material is completely accessible to the acid.¹²

Alcoholysis

The rate of alcoholysis of disordered cellulose was compared with that of ordinary, partially crystalline celluloses.¹⁶ The ethanolysis was carried out in 30% (w/w) sulfuric acid-ethanol at 80°C. for various lengths of time, the residues being washed in ethanol at room temperature; the loss of weight of the cellulose was thus obtained as a function of time of treatment. After 18 hr. treatment the amount dissolved was considerably greater with disordered cellulose than with partially crystalline celluloses.

The rate of ethanolysis of disordered cellulose is found to depend markedly on the way in which the ethanol (used in the preparation) is evaporated from the film: film freed from ethanol at 105°C. is much more reactive than that dried at room temperature. This different reactivity is not associated with any difference in order measurable by infrared-deuteration (not more than 3% order in any sample), or with any significant difference in the "internal surface" of the disordered cellulose, as measured by the nitrogen sorption technique and a non-aqueous oxidation technique (see below). The structural origin of this differing reactivity is thus not fully understood.

Reaction with Formaldehyde in Non-aqueous Solvent

Disordered cellulose fabric was prepared by the non-aqueous saponification of a fabric woven from a cellulose acetate (Tricel) filament yarn. This fabric was crosslinked with formaldehyde in acetic acid (a non-aqueous solvent had to be employed to prevent crystallization of the cellulose); the reaction mixture was 50 g. formalin, 51.5 g. concentrated hydrochloric acid, 170 g. acetic anhydride, 228.5 g. glacial acetic acid, at room temperature. The reacted cellulose was washed in water at room temperature and dried in air. The amount of formaldehyde in the washed and dried samples was determined colorimetrically.¹⁷

Figure 2 shows that the disordered cellulose fabric reacts with much more formaldehyde than does this fabric after crystallizing in boiling water, thus confirming further the highly accessible nature of the disordered cellulose. There is clearly, however, no linear relation between formaldehyde content and the fraction of hydrogen-bond disordered cellulose: the disordered fabric should be only about a third more reactive than the boiled fabric in any simple proportionality with hydrogen-bond disorder.

Measurements of the Internal Surface of Disordered Cellulose

Samples of disordered cellulose were studied by the nitrogen sorption technique and by oxidizing with chromium trioxide in acetic acid-acetic anhydride mixtures;¹⁸ both of these techniques measure the surface area, rather than the molecular disorder, in cellulose. These investigations¹⁶ show that the internal surface of disordered cellulose, i.e., the surface area of internal voids, capillaries, and fibrillar structures, is as small as that of ordinary regenerated celluloses (less than 1 m.²/g.). Thus the high reactivity of disordered cellulose is not merely a surface-area effect associated with the fact that the material is dried from a non-aqueous solvent (it is well known¹⁸⁻²⁶ that celluloses of high internal surface area can be prepared by solvent-drying techniques).

Mechanism of Formation of Disordered Cellulose

It is necessary to discuss the possible reasons why the regeneration of a cellulose by a non-aqueous treatment should give a product consisting almost entirely of hydrogen-bond disordered regions.

One possibility is that molecules of the regenerating agent (e.g., sodium hydroxide), the non-aqueous solvent (e.g., ethanol), or both, remain in the cellulose structure after the washing and drying treatments and, by their presence, prevent the formation of an ordered hydrogen-bonding system.

The amount of residual sodium hydroxide in disordered cellulose prepared from cellulose acetate was measured by leaching out the samples in boiling water. Less than 0.1% by weight of residual alkali was present, provided that the wash in ethanol was sufficiently prolonged. The amount of residual ethanol in a dry, disordered cellulose was estimated in two ways. First, by measuring the oven-dry weight of a cellulose before and

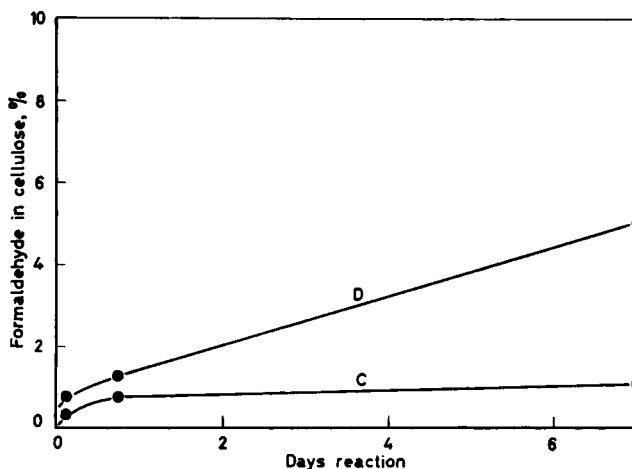


Fig. 2. Uptake of formaldehyde by disordered cellulose: (D) fabric of disordered cellulose; (C) fabric of partially crystalline cellulose.

after extraction with boiling water. Second, by measuring the intensity of the sharp infrared band near 2980 cm.^{-1} due to the ethanol. These measurements indicate that disordered cellulose prepared from cellulose acetate contains about 3–5% by weight of ethanol that is very resistant to evacuation through a liquid nitrogen trap, or to dry heat at 100°C . This trapped ethanol is, however, readily removed by allowing the disordered cellulose to stand for a day or so in an ordinary laboratory atmosphere or for a few hours in 75% R.H. water vapor in the absence of air. The disordered nature of the cellulose is not affected by the removal of this final few per cent of ethanol.

It may thus be concluded that the presence of "foreign" molecules in the structure is not essential to the existence of disordered cellulose, although they may have a minor effect upon structure in some cases.

The essential factor in the formation of disordered cellulose would appear to be the non-aqueous nature of the preparative treatments. The presence of water seems to be necessary for the ready formation of regions of hydrogen-bond order (as was emphasized by Manley^{7,8}); formic acid and dimethylformamide, the only other liquids found to produce hydrogen-bond order, are less efficient in this respect than water. The water may act in two ways; first, as a lubricating agent, facilitating easier chain rearrangements; second, the water may exert a specific ordering effect on the hydrogen-bond structure, as a result of the small size of the water molecule allied to its ability to form two hydrogen bonds. It was thought that a further factor might have been the effect of the high surface tension of water during the drying of the cellulose; this high surface tension could have had the effect of closing capillaries and voids present in the swollen structure, and sealing together cellulose interfaces, to an extent greater than would be the case with a solvent of lower surface tension.²⁶ However,

there is evidence (from the deuteration of never-dried celluloses, and from the small effect of solvent-drying on the hydrogen-bond order in celluloses¹³) that with ordinary, partially crystalline celluloses at least 80% of the hydrogen-bond order in the dried cellulose is present in the never-dried, water-swollen state, i.e., the drying process causes little increase in the hydrogen-bond order.

STABILITY AND CRYSTALLIZATION OF DISORDERED CELLULOSE

Disordered celluloses are stable more or less indefinitely in anhydrous conditions, and are stable for several weeks at least in an atmosphere of about 50–60% R.H. As was mentioned above, however, saturated vapor of deuterium oxide tends to crystallize the disordered cellulose into the cellulose II form.

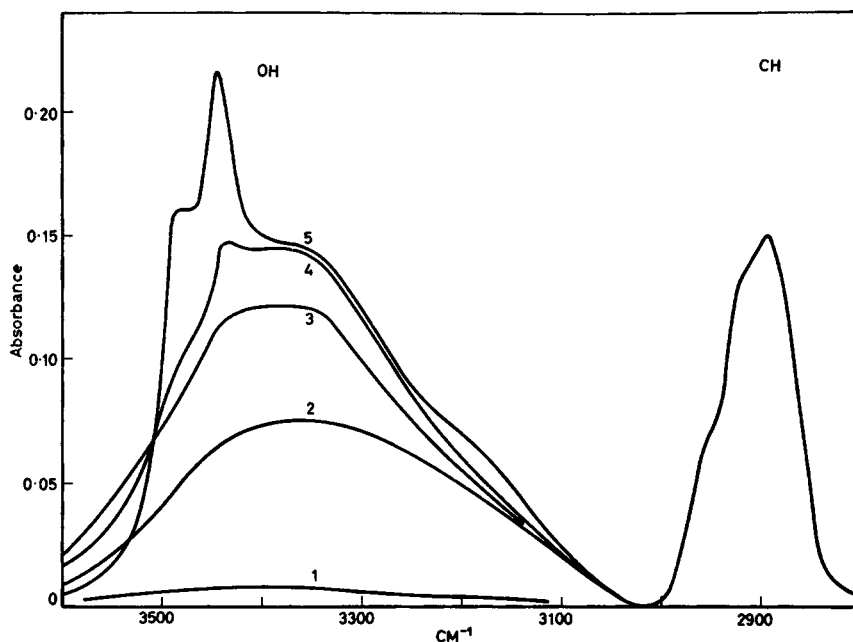


Fig. 3. Treatment of disordered cellulose film in ethanol-water mixtures: (1) ethanol (as prepared); (2) 90/10 (v/v) ethanol-water; (3) 70/30 (v/v) ethanol-water; (4) 50/50 (v/v) ethanol-water; (5) water. All treatments for 30 min. at 25°C. followed by drying in air. The OH bands shown are of the hydrogen-bond ordered regions, the absorption of the disordered regions having been removed by deuteration.

As would be expected from this instability in saturated heavy water vapor, disordered celluloses were found to crystallize very readily in liquid water. A few seconds immersion at room temperature produces about 15% of ordered cellulose of the cellulose II type; treatment in boiling

water produces 20–30% of ordered material, i.e., similar to regenerated cellulose produced in normal aqueous treatments (Fig. 1).

The crystallization of disordered cellulose in mixtures of ethanol and water at 25°C. has also been studied. Two sets of samples were investigated; the first set was dried directly from the ethanol–water mixture; the second set was given a final wash in ethanol before being dried in air. The two sets gave similar infrared-deuteration results. Increasing the proportion of water in the range 0–50% (v/v) causes a gradual increase in the proportion of deuteration-resistant material from about 10% in mixtures containing 10% of water to about 25% (i.e., similar to that produced in

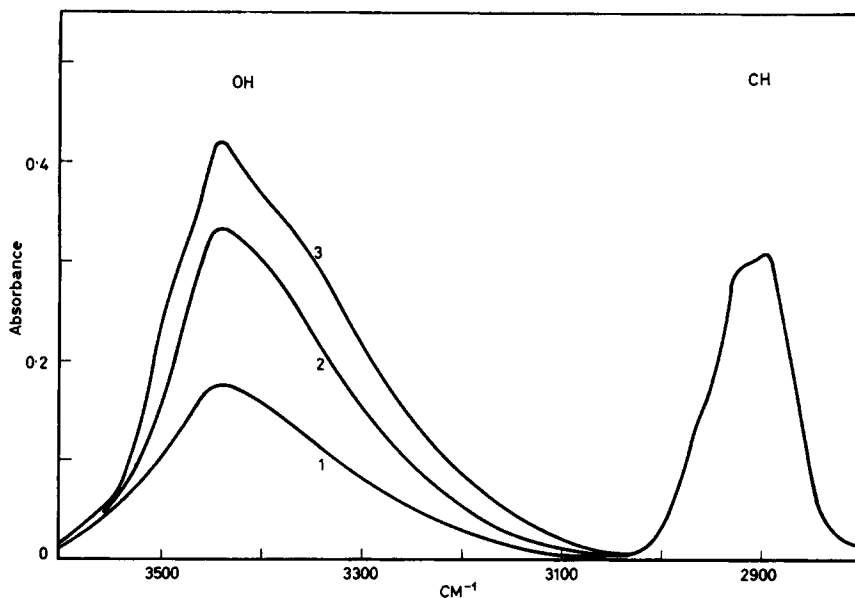


Fig. 4. Treatment of disordered cellulose film in acidified dimethylformamide: (1) Treated in acidified DMF, washed in DMF, and dried; (2) as (1), followed by treatment in cold water and redrying; (3) as (1), followed by treatment in boiling water and redrying. The OH bands are of the hydrogen-bond ordered regions, the absorption of the disordered regions having been removed by deuteration.

pure water) in mixtures containing 50% water. The shape of the hydroxyl band of the deuteration-resistant regions changes in resolution and shape as the concentration of water is increased. With some samples of disordered cellulose (though not with all) the changes in band shape are as pronounced as shown in Figure 3; as the concentration of water is increased the shape of the hydroxyl band of the deuteration-resistant material changes progressively from the broad, poorly-defined band shown in spectrum 2 on Figure 3 to a typical cellulose II band (spectrum 4 is clearly cellulose II in character). These changes may reflect a gradual increase in the perfection of the hydrogen-bond ordered regions.

Treatment of never-dried disordered cellulose with dimethyl-formamide acidified with nitric, hydrochloric, or sulfuric acid (1–4% by volume of acid), followed by washing in DMF or ethanol and drying, gives a product containing 5–10% of a hydrogen-bond ordered (deuteration-resistant) component (Fig. 4). Treatment of this acid-DMF treated film with water at about 20°C. gives a film which after drying contains about 20% of deuteration-resistant OH groups (Fig. 4). Treatment in boiling water usually produces rather more ordered material (probably about 25%). The shape of the hydroxyl band of this ordered component (Fig. 4), and a preliminary x-ray investigation¹⁵ suggest that the ordered material in the water-treated samples may be mainly cellulose IV in character. Mann and Marrinan²⁷ suggested that the hydroxyl band of the ordered regions of a cellulose IV sample prepared by treating cellulose II films in hot glycerol contains some cellulose II shape resulting from residual cellulose II in the structure. The present results tend to support this suggestion; the OH band in Figure 4 (curve 2) is very similar to the band given by Mann and Marrinan²⁷ minus a cellulose II component, indicating that the present material may be a purer form of cellulose IV than Mann and Marrinan's sample. It may be noted that some water-treated samples, particularly if boiling water is used, do contain distinct signs of a cellulose II component on the hydroxyl band of the ordered regions (curve 3, Fig. 4).

The effect of washing the never-dried disordered cellulose in dimethyl-formamide alone is at most small, i.e., it is necessary to acidify the amide to produce these unusual crystallizing effects to any marked extent. However, acidified ethanol had no effect on the never-dried disordered film and it, cannot, therefore be the acidity alone of the acidified DMF treatment that is instrumental in producing the above-described crystallization effects. Acidified dimethylacetamide behaves similarly to the acidified DMF.

TREATMENT OF ALKALI-SWOLLEN CELLULOSES WITH ETHANOL

Alkali solutions of sufficiently high concentration penetrate and swell the crystalline regions of celluloses; the hydrogen bonds in these regions are probably broken and replaced by cellulose-water and cellulose-alkali interactions to give soda celluloses. It was of interest to investigate the effect of washing these swollen celluloses in non-aqueous liquids, e.g., ethanol, to see whether the crystalline hydrogen-bonding system would re-form under these conditions or whether, in the absence of water, a more hydrogen-bond disordered structure would be produced.

Infrared-deuteration studies on bacterial cellulose (swollen in 5*N* sodium hydroxide at 20°C.) and regenerated viscose film (swollen in 2–3*N* sodium hydroxide) showed that washing the alkali-swollen cellulose in ethanol gave a more hydrogen-bond disordered structure than washing in water. In the case of the alkali-swollen bacterial cellulose, washing in water produces normal mercerized bacterial cellulose; this usually comprises about 35% of

ordered cellulose, this ordered cellulose being mainly, but usually not entirely, cellulose II in character (see below). If the swollen bacterial cellulose is washed in ethanol a hydrogen-bond ordered fraction of about 5–15% results, this being entirely cellulose II in character to judge from the shape of the OH band of the ordered regions. Similarly, a sample of viscose film (originally containing about 25% ordered material) gives a product containing 5–15% order when swollen in 2–3*N* sodium hydroxide and washed in ethanol. Washing in water gives about 25–30% order. Thus with both types of cellulose the ethanol-washed samples are more disordered than the water-washed, although less disordered than the disordered celluloses prepared by the non-aqueous regeneration of cellulose derivatives.

Extraction of these ethanol-washed samples with water shows that they contain several per cent by weight of sodium hydroxide, even after washing for several days. One possibility that cannot be overlooked, therefore, is that this residual alkali is the reason for the increased hydrogen-bond disorder. This was checked by washing the alkali-swollen cellulose in acidified non-aqueous washes; three washes were investigated, namely, 1% by weight acetic acid in ethanol, 2% hydriodic acid in ethanol, and 2% nitric acid in dimethylformamide, all followed by prolonged washes in the appropriate pure solvent. Extraction of these acid-washed films (after drying) with boiling water indicates that the amount of trapped molecules (alkali, salt, or ethanol) is no more than 2% of the weight of cellulose in any case, and is usually less than 1%. Infrared-deuteration studies show that these acid-washed samples are more hydrogen-bond ordered than samples washed in pure ethanol. Bacterial cellulose treated in this way is found to contain 10–25% order, the values being irreproducible in this range for reasons not understood. These acid-washed samples are thus more ordered than samples washed in pure ethanol, but less ordered than samples washed in water (about 35%). The order in the acid-washed samples appears to be entirely cellulose II in character (to judge from the OH band shape), as with the samples washed in pure ethanol. The alkali-swollen viscose films, after washing in acidified non-aqueous washes, are in general only a little more disordered than the water-washed samples; moreover, the perfection of the crystalline regions of the acid-washed viscose films appear to be as great as that of the water-washed samples (i.e., greater than the perfection of the ordered regions in the films prior to treatment).

It may be concluded, therefore, that most of the increased disorder in the viscose films washed in pure ethanol is associated with the residual alkali in these films. Some of the increased disorder in the bacterial film washed in pure ethanol can perhaps also be attributed to residual alkali, but here other factors must play a more important part than with the viscose, since the acid-washed bacterial films, containing practically no foreign molecules, are considerably more disordered than water-washed films. The reason for this difference between bacterial and viscose film may be associated with the fact that the swelling and washing causes a change from cellulose I to cellulose II with the bacterial cellulose; this may produce

greater opportunities for the introduction of chain disorder when deswelling is effected in the absence of water.

Recent work on cotton at this Association confirms qualitatively the results obtained with bacterial cellulose, i.e., samples treated in 5*N* sodium hydroxide at 20°C. and then washed in pure ethanol tend to be more hydrogen-bond disordered than equivalent samples washed in acidified non-aqueous solvents, which in turn tend to be more disordered than water-washed samples. However, the level of disorder in the samples washed with non-aqueous solvent appears to be in general rather less than that achieved with bacterial cellulose, i.e., 15–25% ordered regions with pure ethanol, 0–35% with acidified solvents, and 35–40% with water.

A point worthy of special emphasis is the fact that whereas many of the water-washed bacterial cellulose samples, and all of the water-washed cotton samples (i.e., samples swollen in alkali of mercerizing strength and washed free from alkali in water), contain a fraction of cellulose I in the ordered regions (as much as 10–50% of the latter), the alkali-swollen samples washed in non-aqueous media contain ordered regions that appear to be entirely cellulose II in character. The reason for the incomplete cellulose I→II transition of the water-washed samples is not fully understood; it should be emphasized that the swelling and washing treatments were completely without tension, and that the effect is independent of alkali concentration in the range of 5–10*N* sodium hydroxide, at least at 20°C. The effect of the non-aqueous wash in promoting complete mercerization is also difficult to understand. However, it does at least suggest that the alkali treatment penetrates all of the ordered regions of the cellulose and that the cellulose I component in water-washed samples is not merely cellulose I material that is not penetrated or affected by the alkali swelling.

MECHANICAL AND SWELLING METHODS OF INCREASING THE HYDROGEN-BOND DISORDER IN CELLULOSE

This section describes briefly the effects of grinding and of various swelling treatments on the hydrogen-bond disorder in cellulose. Little information on this is available in the literature, although the effects of these treatments on disorder as measured by other techniques have been studied by many workers (grinding^{28–39}; swelling⁴⁰). The purpose of this section is to compare the disorder produced with the disorder present in the non-aqueously-regenerated celluloses described above. The study of grinding was made on cotton; the swelling treatments were all on films of bacterial cellulose.

Grinding of Cotton

Samples of cotton were ground for various lengths of time in a vibrating ball mill (agate balls), and the ground fibers pressed into disks for infrared-deuteration study. This type of milling gradually decreases the fraction of hydrogen-bond ordered (deuteration-resistant) material in the fiber (Fig. 5); a sufficiently prolonged treatment removes practically all hydro-

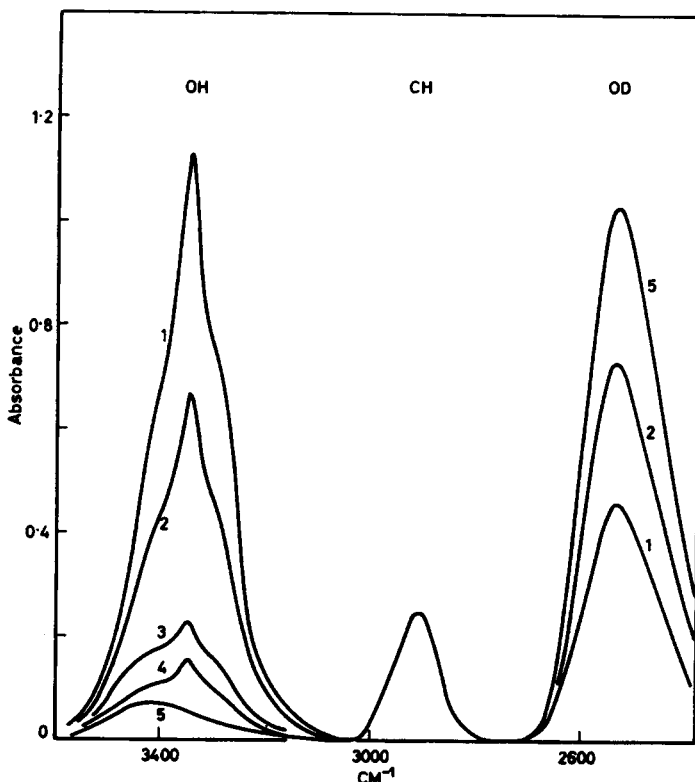


Fig. 5. Effect of ball-milling on the hydrogen-bond order in cotton: (1) unmilled cotton; (2) 20 min. milling; (3) 60 min. milling; (4) 120 min. milling; (5) 240 min. milling. Samples deuterated for 5 hr. at 20°C. in 57% R.H. D_2O vapor and dried, i.e., disordered regions deuterated.

gen-bond order. This increase in disorder is shown by all methods of measurement of disorder.²⁸⁻³⁹ The disordered material produced has a hydroxyl-stretching band similar in shape and peak frequency to that of the disordered regions of unmilled cotton. The hydroxyl band of the deuteration-resistant material shows a gradual change in shape after the more prolonged milling treatments (see curves 3, 4, and 5 on Fig. 5). After 4 hr. milling the small deuteration-resistant component has a band shape (curve 5) that is quite different from that of cellulose I. Curves 3 and 4 suggest that after 1 hr. and 2 hr. milling the band shape of the deuteration-resistant regions is a mixture of the cellulose I band shape and the band shape shown on curve 5. Mercerized cotton milled for 4 hr. also gives an OH band after deuteration of the disordered regions similar to that given by heavily milled cotton (curve 5, Fig. 5). This deuteration-resistant component in heavily milled fibers amounts to no more than 5% of the cellulose. The fact that it is resistant to deuteration and has a band shape different from that of hydrogen-bond disordered cellulose suggests that the hydrogen bonding in these regions must be to some extent

regular and ordered; these regions may contain an imperfect cellulose II lattice, resulting from the presence of atmospheric water vapor during the milling.

Effect of Swelling Treatments on Bacterial Cellulose

The evidence available in the literature indicates that swelling a native cellulose strongly enough to penetrate the ordered regions, followed by removal of the swelling agent and drying, gives a product of a lower degree of order, and of a greater accessibility to reagents of the swelling type, than the original cellulose. A change in the nature of the crystalline material is also sometimes produced: mercerization treatment⁴⁰ and swelling in nitric acid solutions⁴¹ cause a high degree of conversion of cellulose I to cellulose II; treatment in calcium thiocyanate⁴² solutions is also thought to cause some cellulose I→II transition; treatment with ethylamine gives a product with either cellulose I or cellulose III ordered regions, depending upon the method of removal of the amine;^{40,43,44} zinc chloride solutions do not lead to any change in crystalline type, though they do increase the disorder in the native cellulose⁴⁵⁻⁴⁹

In the present investigation, the effects of swelling in aqueous solutions of sodium hydroxide, nitric acid, sulfuric acid, calcium thiocyanate, and zinc chloride, in ethylamine and ethylenediamine, and in solutions of potassium hydroxide in butanol and in butanol-kerosene have been studied. Details of the swelling treatments and the infrared-deuteration results on the treated samples are listed in Table I, samples 16 and 19-27. The results refer to the samples freed from swelling agent; the samples swollen in alkali, acid, or salt solutions were washed in water at 20°C. and dried in air; the ethylamine was removed either by washing in chloroform (followed by drying in air) or by evaporation; the ethylenediamine was removed first by evacuation (to give the amine-cellulose complex) and then by extraction in water or dimethylformamide; the potassium hydroxide was removed by washing the swollen samples in acidified ethanol and then in pure ethanol, followed by drying in air. It is clear that all these swelling treatment (with the exception of the zinc chloride) produce a marked increase in the fraction of hydrogen-bond disordered cellulose in the bacterial film, in broad agreement with the published results obtained with other techniques for measuring disorder. However, in no case was the disorder raised to a level approaching the 97-100% characteristic of disordered cellulose produced by the non-aqueous regeneration techniques described above. The effect of the various swelling treatments on the type of the remaining ordered regions is also in general as expected from the literature. There are, however, a number of points worthy of special note, as follows.

The effect of swelling in aqueous sodium hydroxide solutions, followed by washing in water, has been studied in more detail than indicated in Table I, a range of alkali concentrations and temperatures having been investigated. Up to a certain concentration of alkali, depending upon the

temperature, the treated films are indistinguishable, as regards infrared-deuteration behavior, from the original films. Above this concentration, a gradual increase in the fraction of hydrogen-bond disordered cellulose, and a gradual change in the lattice type of the ordered fraction (from cellulose I to cellulose II), are produced. The shapes of the OH bands of the ordered regions of partially mercerized samples are similar to bands constructed by adding together various proportions of the cellulose I and cellulose II shapes and confirm that the ordered regions of partially mercerized samples are probably mixtures of cellulose I and cellulose II components. At a higher concentration, again depending upon the temperature of swelling, these effects of mercerization level out. At this "equilibrium" stage, the percentage of disordered cellulose has increased from 35%³ to about 65%. The degree of conversion of cellulose I to cellulose II at equilibrium is irreproducible; in a few cases the conversion is complete but in others a considerable fraction (as much as a half, but usually about a fifth) of the ordered regions is still in the cellulose I form. This incomplete conversion of the crystalline arrangement, discussed in an earlier section and noted previously by Rånby,⁵⁰ cannot be explained with any certainty, nor can the marked irreproducibility. The effect of increasing the temperature of the swelling treatment was as expected, i.e., the approximate range of alkali concentrations over which the mercerization effects take place was increased from 8–12 g./100 ml. at 0°C. to 13–20 g./ml. at 25°C. and to 18–25 g./100 ml. at 50°C.

The cellulose I ordered regions present in amine-treated samples from which the amine has been removed by extraction are not hydrogen-bonded in the same way as the cellulose I regions in the original bacterial cellulose. The hydroxyl-stretching band of the ordered regions of the treated films appears to be similar to the type B variety described by Mann and Marrian,²⁷ whereas that of the original film is of the type A variety.

Treatment in concentrated solutions of sulfuric acid (as is done in parchmentizing processes⁵¹) is seen to increase the hydrogen-bond disorder; the hydroxyl band of the remaining ordered regions is rather similar in shape to that given by cellulose II ordered regions, though blurred in character.

The reason why zinc chloride solutions have no apparent effect on bacterial cellulose, although there is much evidence of a considerable effect on cotton,^{45–49} is possibly explicable in terms of the rather greater perfection of the ordered regions in bacterial cellulose, and emphasizes that bacterial cellulose is not suitable as a model for cotton for all types of swelling system.

The effect of swelling in solutions of potassium hydroxide in butanol, or butanol-kerosene,⁵² followed by washing in acidified ethanol, is rather similar as regards infrared-deuteration to the effect of certain types of amine treatment, i.e., there is an increase in the hydrogen-bond disorder and a change in the remaining cellulose I regions from type A hydrogen bonding to type B. It should be emphasized here, however, that this swelling system is complex in nature, since there is strong evidence that the swelling

effects described are associated with the hazy material generally found in solutions of potassium hydroxide in butanol, even with reagents of analytical quality.

General Conclusions

It is clear from the above study of the hydrogen-bond disorder produced by various swelling systems that none of these systems produces a cellulose as highly disordered as the cellulose produced by the non-aqueous regeneration method. Only grinding for prolonged periods can give a product with a degree of hydrogen-bond disorder as high as 95%; the present results, however, indicate that even prolonged grinding does not completely remove the hydrogen-bond order, and in any case ground cellulose is unsuitable for many types of physical measurement.

POSSIBLE TECHNOLOGICAL UTILIZATION OF DISORDERED CELLULOSE

The work carried out on the possible commercial utilization of disordered cellulose, as produced by non-aqueous regeneration methods, will be described briefly.

The first possible use was based on the high accessibility of disordered cellulose to chemical reagents. It was thought that if a crosslinking agent could be reacted throughout the cellulose structure, then a product with desirable crease-resistant properties might result. The non-aqueous crosslinking system described above (formaldehyde in acetic acid-acetic anhydride) was chosen for study. Increasing the duration of this crosslinking treatment given to the disordered cellulose fabric is found to produce a steady rise in the crease resistance of the fabric. However, the samples prepared from the disordered fabric are at no stage more crease-resistant than the equivalent samples prepared from a "crystalline" fabric (i.e., disordered fabric boiled in water and dried prior to the crosslinking treatment). This is so even when the crosslinked disordered fabrics are subsequently boiled in water to crystallize them and is difficult to understand, particularly since the disordered fabric has a larger uptake of formaldehyde than the "crystallized" fabric (Fig. 2). It may be that the crosslinks in the disordered fabric prevent or modify to some extent the subsequent crystallization in the boiling water. Such a retention of a high state of disorder would certainly explain the poor crease resistance, since disordered fabrics prior to crosslinking have a very poor crease recovery.

The second potential technological use of disordered cellulose depends upon the marked crystallizing effect of water. It was thought that yarn or fabric of disordered cellulose could be "set" into a particular preformed shape by means of this crystallizing action. The setting of pleats in fabrics by this method has been studied. The fabric was pleated in the disordered state and the pleats were set in by treatment of the fabric in hot water. The pleats set in this fashion proved to be very resistant to boiling and ironing treatments.

The third possible use of disordered cellulose is based upon the practically complete lack of hydrogen-bond order, and the very poor lateral order, of disordered cellulose. It was hoped that by "crystallizing" this disordered cellulose in a variety of ways it might be possible to produce a cellulose with desirable mechanical properties, e.g., a high strength. The crystallization of "disordered" filament yarn in a variety of crystallizing agents, including water at various temperatures and mixtures of water and organic reagents, has been studied; however, no crystallizing treatment so far tried has produced any marked or desirable change in mechanical properties.

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